

It will be readily understood that the bands can be measured with far less accuracy than lines, and that they are subject to some degree of variation in width, according to variation in the time of exposure and the temperature.

A striking group of lines, the most persistent in the whole of these spectra, is situated in the violet. The following measurements were made:—

4036·5	4034·9	Ångström, also Cornu.
4032·0	$\left\{ \begin{array}{l} 4032·9 \\ 4031·8 \end{array} \right\}$	Ångström.
4029·5	4029·4	Ångström.

Another line is just visible about 4031·8, but it is so close to 4032·0 that it could be discerned only when the extreme points of three very strong lines were examined, and the plate was in perfect focus for that region. The whole group of lines appears as two bands very closely adjacent, or in the manganese oxide spectrum as one band with the centre appearing as if reversed, the less refrangible edge of the band being very strong and sharp, the more refrangible being degraded and diffuse. These lines remain after the bands in the yellow and green have disappeared from the photographs, but the result may be quite otherwise with eye observations, owing to the greater visibility of the yellow over the violet rays.

Photographs of the spectra obtained with a dispersion of four quartz prisms of 60°, and lenses of 15 inches in focal length, are presented with the paper.

V. "Flame Spectra at High Temperatures. Part III. The Spectroscopic Phenomena and Thermo-Chemistry of the Bessemer Process." By W. N. HARTLEY, F.R.S., Royal College of Science, Dublin. Received May 4, 1894.

(Abstract.)

The flame issuing from the mouth of a Bessemer converter was first investigated by Sir Henry Roscoe* in 1863; by Lielegg,† and by Marshall Watts in 1867;‡ by Tunner,§ J. M. Silliman, Rowan,|| Von

* 'Literary and Phil. Soc., Manchester, Proc.,' vol. 3, p. 57, and 'Phil. Mag.,' vol. 34, p. 437.

† 'Sitzungsberichte Kaiserl. Akademie der Wissenschaften,' Wien, vol. 56, Part II.

‡ 'Phil. Mag.,' vol. 34, p. 437.

§ 'Dingler's Polytech. J.,' vol. 178, p. 465.

|| 'Phil. Mag.,' vol. 41, p. 1.

Lichtenfels,* Spear Parker,† Kupelwieser,‡ Brunner,§ and Wedding in 1868 ;|| also by A. Greiner in 1874.¶

Up to the present time the precise nature of the spectrum, the cause of its production, its sudden disappearance when decarburization of the metal takes place, and the connexion between the decarburization of the metal and the extinction of the spectrum, have not been satisfactorily explained. According to Roscoe, Lielegg, Kupelwieser, and Spear Parker, the spectrum is characterised by bands of carbon or of carbon monoxide, which disappear when all carbon is burnt out of the metal.

On the other hand, according to the investigations of Simmler,** Brunner, Von Lichtenfels, and Wedding, the spectrum is not due to carbon (Roscoe) or to carbon monoxide (Lielegg and Kupelwieser), but to manganese and other elements in the pig-iron.

The very careful examination of these spectra by Watts and his comparison of them with that of the Bessemer flame led to the conclusion that it was not the spectrum of carbon in any form nor of manganese, but that of manganic oxide. Lielegg established the fact that carbon monoxide yields a continuous spectrum, and that this gas causes the continuous bright spectrum of the Bessemer flame; but he also attributed certain lines or bands to the high temperature of the carbon monoxide. All observers are agreed as to the appearance after a certain interval of the lines of the alkali metals which were originally discovered by Roscoe to be present during the first period of the "blow." Watts observed the C line of hydrogen during wet weather.

This research was undertaken in 1882, and an instrument was devised for the purpose of photographing the spectra of various flames emitted during metallurgical operations. The work was left in abeyance until certain practical difficulties encountered in studying flame spectra at high temperatures in the laboratory had been overcome. The original mounting of the instrument was too light, but that which has recently been used with success is described.

Owing to the courtesy of Mr. F. W. Webb, the engineer of the Locomotive Department of the London and North Western Railway, and of Mr. E. P. Martin, the manager of the Dowlais Ironworks, observations have been made at Crewe and at Dowlais during the past year. About ninety spectra were photographed, about fifty of which were available for study.

* 'Dingler's Polytech. J.,' vol. 191, p. 213.

† 'Chem. News,' vol. 23, p. 25.

‡ 'Oesterreichische Zeitschr. für Berg- und Hütten-Wesen,' No. 8, p. 59, 1868.

§ *Loc. cit.*, No. 29, p. 227, 1868.

|| 'Zeitschrift für das Berg- Hütten- und Salinen-Wesen,' vol. 27, p. 117, 1869.

¶ 'Revue Universelle,' vol. 35, p. 623.

** 'Zeitschr. für Analytische Chemie,' 1862.

The spectra studied extended from the red potassium line $\lambda 7697$, and on some of the plates to about the line P on Cornu's map of the solar spectrum, $\lambda 3380.8$; but the least refrangible line photographed was that of lithium $\lambda 6707$. The bands and lines in various spectra taken at Crewe and Dowlais have been measured, and their wave-lengths determined. Descriptions of the spectra and how they were obtained are given. The description of each band and line measured is given, with its wave-length, its origin, and other references. Photographs of the spectra are presented, and a map has been drawn for the identification of the lines on these photographs. About ninety-two lines were identified with lines in the solar spectrum, with lines in Kayser and Runge's map of the arc spectrum of iron, and on spectra from steel and ferric oxide heated in the oxyhydrogen flame.

The Constitution of the Bessemer Spectrum.

The spectrum is a complex one which exhibits differences in constitution during different periods of the "blow," and even during different intervals in the same period. As originally observed by Watts, the spectrum differs in different works, the difference being due to temperature and to the composition of the metal blown.

During the first period.	{ The lines of the alkali metals, sodium, potassium, and lithium, are seen unreversed on a bright continuous spectrum caused by carbon monoxide. The C line of hydrogen and apparently the F line were seen reversed during a snowstorm.
During the second period. The "boil."	{ Bands of manganese are prominent, overlying the continuous spectrum of carbon monoxide. There are lines of carbon monoxide, manganese, and iron, also those of the alkali metals.
During the third period. The "fining stage."	{ The spectrum is the same as the foregoing, but the lines of iron are not so strong and not quite so well defined. Some of the short lines disappear. The lines of the alkali metals are visible.

It is also probable that some of the bands of manganese oxide are present, but they are obscured by the continuous carbon monoxide spectrum. No absorption bands were seen, no nitrogen bands, nor bands of calcium and magnesium oxide, neither did the lines of these metals appear. There is no trace of cobalt, nickel, chromium, or copper; certain carbon bands overlies those of manganese, and are recognised by measurements of their edges. Some of the lines not identified by Watts prove to be iron lines, others belong to manganese. The manganese bands are all degraded towards the red, the carbon bands towards the blue.

The cause of the Non-appearance of Lines at the Commencement and Termination of the "Blow."

Some controversy followed upon the publication of the papers by Roscoe and Lielegg. Tunner stated that in Sweden the Bessemer process was not facilitated by the use of the spectroscope. Brunner pointed out that the spectroscopic phenomena were not dependent on the combustion of carbon, but were characteristic of the various impurities in the metal. Wedding and Silliman discussed the origin of the spectrum seen at different periods of the "blow," and failed to account fully at that time for the non-appearance of lines at its commencement and termination. Their views did not harmonise. Many facts were discovered which were not understood, appeared contradictory, and required verification. These have all been carefully examined and accounted for.

Support is given to Wedding's view, based on the analyses of Brunner, that the non-appearance of the lines of manganese at the commencement and termination of the blow is owing to the quantity of metal volatilised at those periods being insufficient for the production of a spectrum. At the commencement the temperature is too low, being very little above that of the molten metal; and, as free oxygen escapes along with carbon dioxide, the gaseous mixture contains too small a proportion of carbon monoxide. The alkalis which come from the ganister lining of the converter are present as silicates, and in very small proportion; many silicates, such as, for instance, felspar, do not exhibit spectra of the alkalis they contain until heated in the oxyhydrogen flame, but at this temperature the metals potassium, lithium, and rubidium have been detected with the greatest ease in such silicates. Similarly, the alkali metals do not show themselves in the Bessemer flame until a layer of slag has been formed, and the temperature has risen sufficiently high for these basic constituents to be vaporised. At the temperature of the "boil," or second period, both metallic manganese and iron are freely vaporised in a current of carbon monoxide, which, in a highly heated state, rushes out of the bath of molten metal. The evidence of this is the large number of bands of manganese and lines of iron in the spectrum.

When the metal blown contains but little manganese, as, for instance, hæmatite pig, this is all converted into silicate during the first period. The manganese spectrum in the flame does not arise from that substance being contained in the bath of metal, it must be vaporised from the slag. That this is so has been proved by photographs of the spectrum from samples of slag obtained from the Crewe works. There is very little difference between these and the photographs of the flame-spectrum taken at Crewe, during the "boil," the

difference being chiefly in the iron line being stronger in the slag spectrum. This explains the fact observed by Brunner, namely, that when a converter is being heated with coke after it has been used, but not re-lined, the spectrum of the Bessemer flame makes its appearance; manifestly it comes from the adhering slag.

The luminosity of the flame during the "boil" is due, not merely to the combustion of highly heated carbonic oxide, but also to the presence of the vapours of iron and manganese in the gas.

The disappearance of the manganese spectrum at the end of the "fining stage," or third period, is primarily due to a reduction in the quantity of heated carbon monoxide escaping from the converter, which arises from the diminished quantity of carbon in the metal. When the last traces of carbon are gone, so that air may escape through the metal, the blast instantly oxidises any manganese, either in the metal or in the atmosphere of the converter, and, furthermore, oxidises some of the iron. The temperature must then fall with great rapidity.

The entire spectroscopic phenomena of the "blow" are undoubtedly determined by the chemical composition of the molten iron, and of the gases and metallic vapours within the converter, the temperature of the metal and that of the issuing gases.

The Temperature of the Bessemer Flame.

The probable temperature of the Bessemer flame at the finish is that produced by the combustion in cold air of carbonic oxide heated to about 1580°C ., that is to say, to the temperature which, according to Le Chatelier ('Comptes Rendus,' vol. 114, p. 670), is that of the bath of molten metal from which the gas has proceeded. The bath of metal acts simultaneously as a means of heating the blast, producing the gas, and as a furnace, on the regenerative principle, which heats the gas prior to its combustion. The heating effect is therefore cumulative. The temperature, as is well known, can easily rise too rapidly, and the metal has then to be cooled by throwing cold pig-iron, or even old ingot moulds, into it.

If we may judge by the lines and bands belonging to iron and manganese which have been measured in photographed spectra of the Bessemer flame, the temperature must nearly approach that of the oxyhydrogen flame, and may easily attain the melting point of platinum, namely, 1775°C . (Violle).

Marshall Watts observed ('Phil. Mag.,' 1870) that the sodium lines 5681 and 5687 may be employed as an index of temperature, since they are present in the spectrum of any flame containing sodium which is hot enough to melt platinum, but do not appear at lower temperatures. The Bessemer flame does not show this double line, but only the D lines.

We cannot, however, conclude from this that the flame is not hot enough to produce these lines, for though the temperature may be high enough the quantity of material present is not sufficient to cause their appearance. Moreover, there are two intensely brilliant bands of manganese closely adjacent, one of which certainly overlies these lines. Lastly, they are not to be seen in the photographed spectrum obtained from slag heated in the oxyhydrogen flame, which melts platinum easily and slowly volatilises iridium wire.

From thermo-chemical data the heat evolved during the "blow" has been calculated, but the specific heats of cast iron, slag, carbon monoxide, and nitrogen are unknown at temperatures between 1200° C. and 2000° C. If we allow for 50 per cent. of the heat developed at high temperatures being lost by radiation or absorbed, then the estimated temperature of the metal in the converter is more than 1900° C.

Le Chatelier ('Comptes Rendus,' vol. 114, p. 670) found the steel in the ladle of a Robert converter to be at 1640° C. Reasons are adduced for believing that it must certainly have been hotter than this at the highest temperature of the "blow."

The Technical Aspect of this Investigation.

The spectrum obtained from Bessemer-slag by the oxyhydrogen flame is composed of precisely the most characteristic features of the flame spectrum, as seen issuing from the converter at Crewe. Hence at this temperature iron and manganese are freely volatilised, as they are in the oxyhydrogen flame. As a matter of course the continuous spectrum of carbon monoxide, the bands and lines of that compound and of elementary carbon are absent from the slag spectrum. The flame spectrum at Dowlais differs from this, and resembles the spectrum of metallic manganese or more closely that of ferro-manganese. For reasons given, I conclude that the spectrum at Crewe results from materials in the slag; but that at Dowlais from constituents vaporised from the bath of metal.

The complete termination of the "fining stage" is clearly indicated, but there is no indication by the flame of the composition of the metal within the converter at any previous stage. As the progress of the "blow" is governed by the composition of the metal and its temperature in the converter, and as these cannot be controlled with perfect exactitude during each "blow," it follows that the practice of complete decarburization* is the best course to pursue, the required

* The words "carburizing" and "decarburizing" are to be preferred to "carbonising" and "decarbonising" when applied to metals, because these expressions were those originally used in the older works on metallurgy, and they avoid confusion with the other signification of the word "carbonising."

amount of carbon and manganese being added subsequently in the forms of grey iron, spiegel, or ferro-manganese.

I propose to continue this work by extending my observations to the flame from the basic Bessemer process and the gases in the Siemens steel furnace.

VI. "On a Method for determining the Thermal Conductivity of Metals, with Applications to Copper, Silver, Gold, and Platinum." By JAMES H. GRAY, M.A., B.Sc., 1851 Exhibition Scholar, Glasgow University. Communicated by LORD KELVIN, P.R.S. Received May 24, 1894.

(Abstract.)

The object of this investigation was to obtain a method for determining thermal conductivities of metals, which would not require either elaborate preparations or large quantities of the substances to be tested, and by means of which a test could be made in a few hours.

The method about to be described was suggested by Lord Kelvin thirty years ago, and is the experimental realisation of the theoretical conditions implied in the fundamental formula

$$Q = kA \frac{v - v_0}{l} t,$$

where the symbols have their usual meaning.

The apparatus was made so as to be suitable to test the metals in the form of wires of circular section.

The diameters found most convenient were [from 2 to 4 mm., the lengths from 4 to 8 cm.

One end of a given length of the wire is kept at a constant known temperature. The rise of temperature of the other end of the wire is noted every minute, and, if proper precautions be taken to prevent loss by radiation from the sides, the data are obtained for calculating the thermal conductivity.

The wire to be tested is soldered at one end into the bottom of a copper box, 16 cm. long, 6 cm. wide, and 7 cm. deep. The bottom of the box is made of copper 3 mm. thick, the sides of thin sheet copper.

In the box, immediately above the hole into which the wire is soldered, there is a large block of copper, in which a hole has been made sufficiently large to admit a small thermometer.

The box is filled with water and supported at its middle by being fitted into an asbestos-lined wooden screen, 24 × 24 cm. The water is heated by a Bunsen burner placed on the other side of the screen